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Removal of Congo Red from Aqueous Solution Using Groundnut Shells

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Abstract—*Congo red is a carcinogenic dye, one of the most common pollutants in water which is found in the effluents of textile and paper industries during rinsing and dyeing processes. This study was carried out for the adsorption of congo red dye from aqueous system using low cost natural adsorbents such as groundnut shells. Since groundnut shells are waste material and a natural adsorbent they are easily obtained from the domestic sources. The effect of various experimental parameters such as pH, contact time, concentration, adsorbent dosage and temperature was investigated using a batch adsorption technique. It was observed that under the optimized conditions the percentage efficiency for the removal of Congo red was upto 83%. Freundlich and Langmuir equations were used to analyze the equilibrium adsorption data. Various thermodynamic parameters such as* $\Delta G°$,$\Delta H°$ *and* $\Delta S°$ *have been calculated.*

1. INTRODUCTION

Industrial wastewaters discharges coloured materials into streams and rivers which constitutes one of the major sources of water pollution. Dye, a coloured constituent is widely used in textile, paper, plastic, food and cosmetic industries. Dyes cause several problems since they are generally stable to light and oxidation and hence they cannot be treated by conventional methods of aerobic digestion[1]. Congo red (1-naphthalenesulfonic acid,3,3'-(4,4'-biphenylene bis(azo)) bis(4-amino-) disodium salt) is a benzidine-based anionic diazo dye. This dye is known to metabolize to benzidine, a known human carcinogen[2]. Physicochemical processes are generally used to treat dyes laden wastewater. These processes include flocculation, electro floatation, precipitation, electrokinetic coagulation, ion exchange, membrane filtration, electrochemical destruction, irradiation and ozonation. However, all these processes are costly and cannot be used by small industries to treat wide range of dye waste water. [3] The adsorption process is the best technique for the removal of dyes from wastewater especially if the adsorbent is inexpensive and readily available.

Activated carbon is the most widely used adsorbent due to its large surface area, microporous structure, and the high adsorption capacity. However its use is limited due to its high cost. This has led to search of cheaper adsorbents. Investigators have studied the feasibility of using low-cost substances [4], such as waste apricot[5], coconut shell[6], dairy sludge[7], bamboo grass treated with concentrated sulfuric acid[8], peat[9], orange peels[10], pea nut hulls[11], rice husk[12], baggase [13], bamboo[14], date stone and palm tree waste as adsorbents for the removal of dyes and metals from wastewater.

The purpose of present work is to study the mechanism of adsorption of Congo red (anionic dye) on groundnut shells. The kinetics, equilibrium and thermodynamic parameters are studied to describe the rate and mechanism of adsorption to determine the factor controlling the rate of adsorption and to find out the possibility of using these biomaterials as low-cost adsorbents for the removal of dye CR (Congo red). The effect of solution concentration, adsorbent dose, contact time, pH and temperature has been evaluated.

2. MATERIAL AND METHODS

2.1 Dye solution preparation

The dye Congo Red (Chemical Formula= $C_{32}H_{22}N_6O_6S_2Na_2$, Formula weight =696.65) was used as such without purification. An accurately weighed quantity of dye was dissolved in double distilled water to prepare the stock solution (10 mg/l).Serial dilutions were made by diluting with double distilled water.

2.2 Adsorbents

Groundnut shells used as an adsorbent was collectively obtained from local shop, washed with distilled water to remove the suspended impurities, dust and soil and dried in oven and then ground to fine particles.

2.3 Estimation of optimum pH

The pH was varied from 2-10 by using 0.1M HNO_3 and 0.1M NaOH. The absorbance was noted using U.V-visible spectrophotometer at 550nm.Then fixed amount of dosage (0.2g) of sorbent was added in each flask. Flasks were then kept in a shaker for 30 minutes at 25°C. After agitation, the solutions were centrifuged to remove colloidal materials and then the absorbance of supernatant solution was noted at 550nm.

2.4 Estimation of optimum Adsorbent dosage

Different amount of adsorbent (0.2g, 0.4g, 0.6g, 0.8g, 1.0g, 1.5g, 2.0g) was taken and the same procedure followed to determine the adsorption.

2.5 Estimation of optimum contact time

With a fixed amount of sorbent (0.2g) the time of contact was changed from 30min, 60min, 90min, 120min, 150min and 180min. The adsorption effect was noted down.

2.6 Estimation of optimum dye concentration

50ml of Congo red solution of different concentrations (0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 6.0) of dye solution and the absorbance was noted at 550nm using UV spectrophotometer.

2.7 Estimation of optimum Temperature

3 different flasks were kept at different temperature (25°C, 30°C, 40°C) and then the absorbance was noted at 550nm using UV spectrophotometer.

2.8 Batch Adsorption studies

The optimization of all parameters and the further studies were done by batch equilibrium method. They were carried out by adding known volume of prepared congo red solution into a number of flasks containing a known amount of adsorbent. The percentage removal of efficiency was calculated by

$$\text{Removal efficiency (\%)} = \frac{ci - cf}{ci} * 100$$

Where, Ci is the initial concentration(mg/l) and C_f is the final concentration (mg/l)

3. RESULTS AND DISCUSSION

Effect of pH: The efficiency of adsorption is dependent on the pH of solution since variation in pH leads to the variation in the surface properties of the adsorbent and the degree of ionization. It was observed that the percentage removal decreases with increase in pH. In this study, the maximum dye removal of 61.3% was obtained at pH 2 with groundnut shells for Congo red. Hence it can be concluded that the acidic range of dye is favourable with groundnut shells.

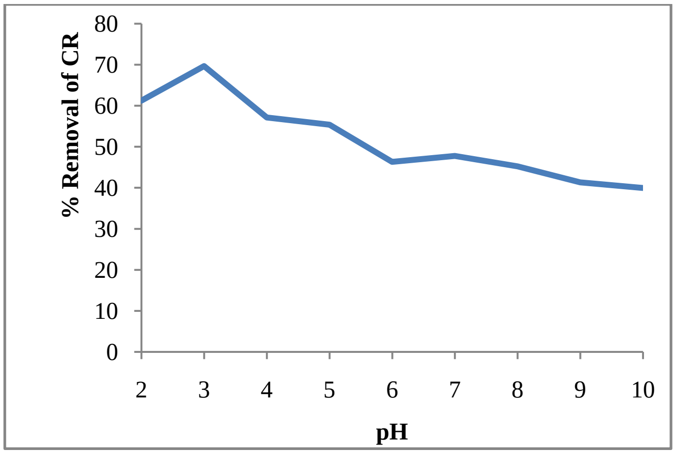

Fig. 1: Effect of pH

Effect of adsorbent Dosage: Removal of colour of dye directly depends on the mass of adsorbent. It was observed that the percentage removal of dye increases with the increase in adsorbent dosage. It is due to the fact that increase in adsorbent dose and surface area also gets increased. In this study, the maximum dye removal of 86.7% was obtained with 0.8g of groundnut shells provides increase in pores available for adsorption.

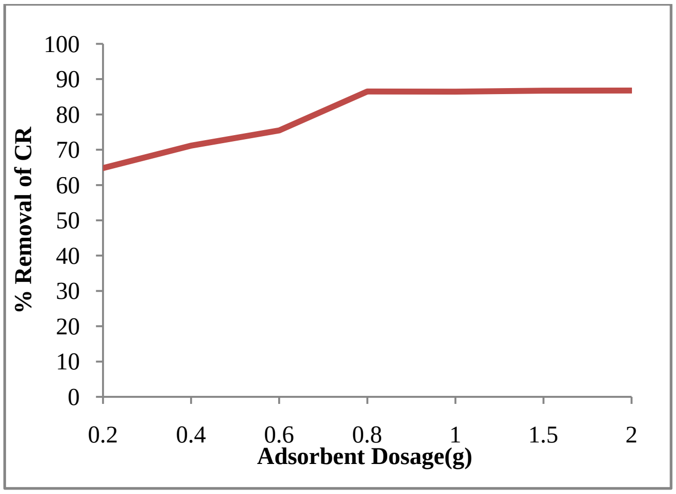

Fig. 2: Effect of adsorbent dosage

Effect of contact time It was observed that as contact time increased the % removal also showed an increase but not to a very large extent.

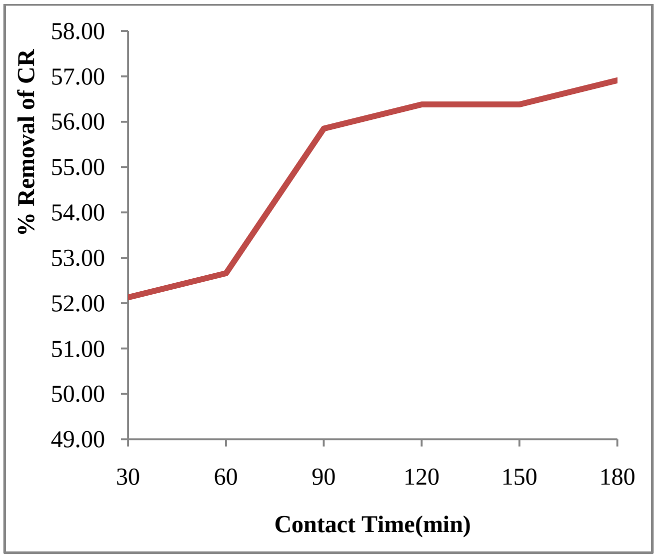

Fig. 3: Effect of contact time

Effect of concentration of dye It was observed that the percentage removal of dye decreases with the increase in concentration of dye. This is due to limited availability of active sites on adsorbent.

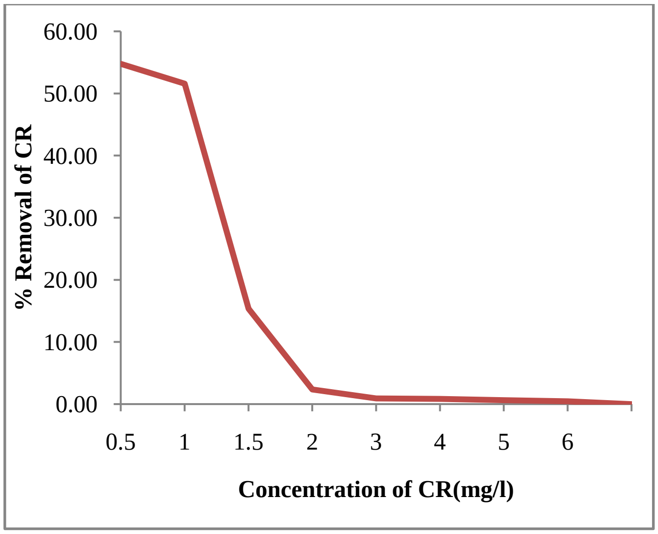

Fig. 4: Effect of concentration of CR

Effect of Temperature It was observed that high temperature favours the high removal efficiency. In this study, the maximum percentage removal was obtained at 40°C

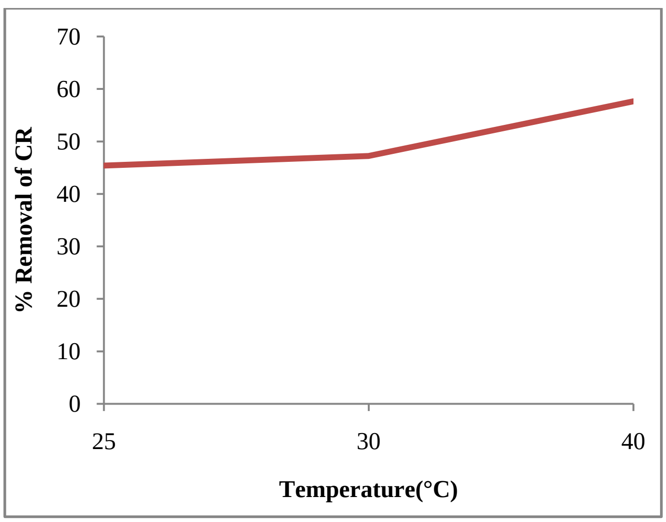

Fig. 5: Effect of temperature

Adsorption Isotherms

Langmuir isotherm: The Langmuir isotherm equation is given as

$$Ce/(qe) = 1/qmK + Ce/qm$$

Here, Ce: equilibrium concentration (mg/l), qe: the amount adsorbed at equilibrium (mg/g).

qm and K are Langmuir constants and are calculated from slope and intercept respectively of the plots (C_e/qe vs C_e)

.**Freundlich isotherm:** The Freundlich equation is:

$$q_e=K_f C_e^{n}$$

Here, q_e: the amount of dye sorbed at equilibrium per gram of sorbent (mg/g) C_e: equilibrium concentration of dye. $K_{f,}$, n are the Freundlich constants. The graph is plotted between q_e and C_e. The Freundlich equation can be rearranged in linearized in logarithmic form in order to determine Freundlich constants. This can be shown as

$$\text{Log}(q_e) = \text{Log}(K_f) + 1/n\ \text{Log}(C_e)$$

K_f and 1/n are Freundlich constant.1/n is heterogeneity factor and K_f indicates the adsorption capacity. The value of n and K_f are calculated from slope and intercepts of the plots of log qe vs log C_e.

Langmuir Isotherm is followed in this adsorption process.

Langmuir Isotherm			Freundlich Isotherm		
R2	Qm (mg/g)	K (L/mg)	R2	Kf	N
0.9826	90.977	151.03	0.8968	1.483	0.9286

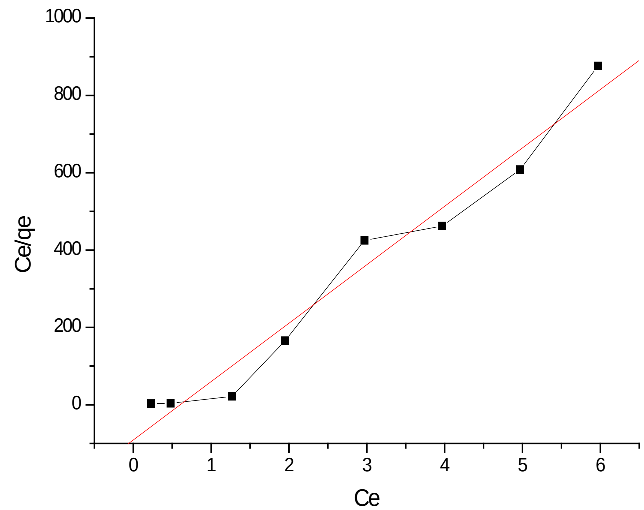

Fig. 6: Langmuir adsorption isotherm

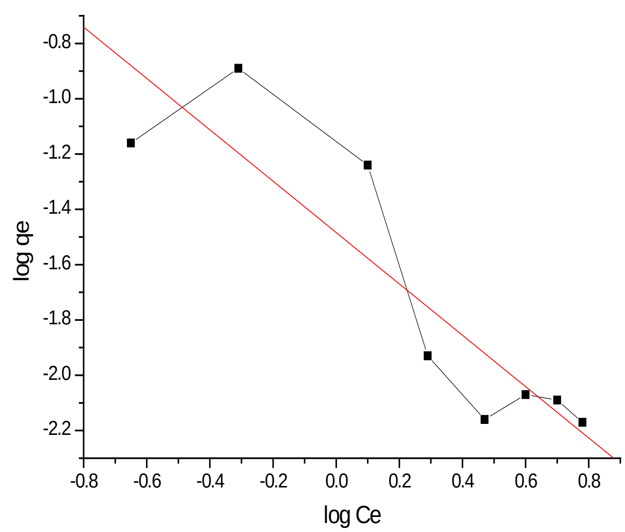

Fig. 7: Freundlich adsorption isotherm

Adsorption Kinetics

Pseudo-first order kinetics: This model was derived by Lagergren. If adsorption continues by diffusion through a boundary, it follows pseudo first order equation.

$$\frac{dqt}{dt} = k_{ad}(q_e - q_t)$$

Where q_e(mg/g) is the adsorption capacity at equilibrium time and q_t(mg/g) is the adsorption capacity at time t..k_{ad}(min^{-1}) is the rate constant. The integrated rate law equation(at qe=0 at t=0) becomes

$$\text{Log}\ (q_e - q_t) = \log q_e - \frac{kad}{2.303}t$$

The rate constant i.e k_{ad} can be computed from the linear plots between log (q_e-q_t) versus t.

Pseudo-second order kinetics: The equation of the pseudo-second order kinetics is:

$$\frac{dqt}{dt} = k_2\ (q_e - q_t)^2$$

Where, k_2 is rate constant(g mg^{-1} min^{-1})·The integrated rate law equation(at qt=0 at t=0) becomes $\frac{t}{qt} = \frac{1}{k2e^2} + \left(\frac{1}{q_e}\right)t$

qe ank k_2 are calculated from slope and intercept from linear plots of t/qt vs t.

Pseudo first order kinetics			Pseudo second order kinetics		
R2	kad	Qe	R2	Qe	K2
0.9328	-0.0064	1.532	0.9998	0.03434	0.154

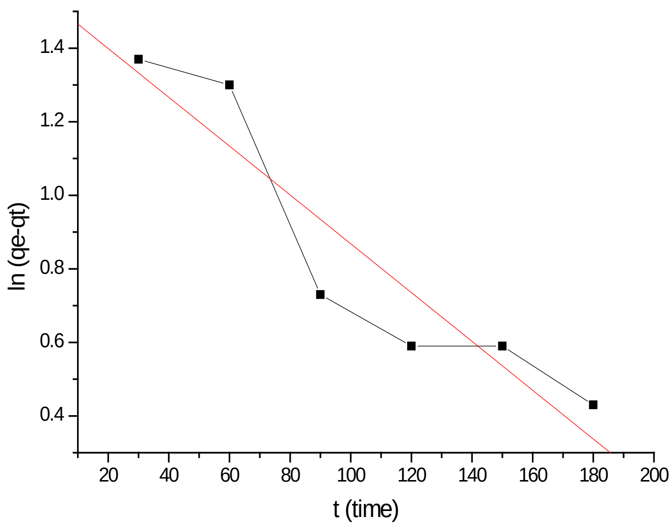

Fig. 8: Pseudo first order kinetics

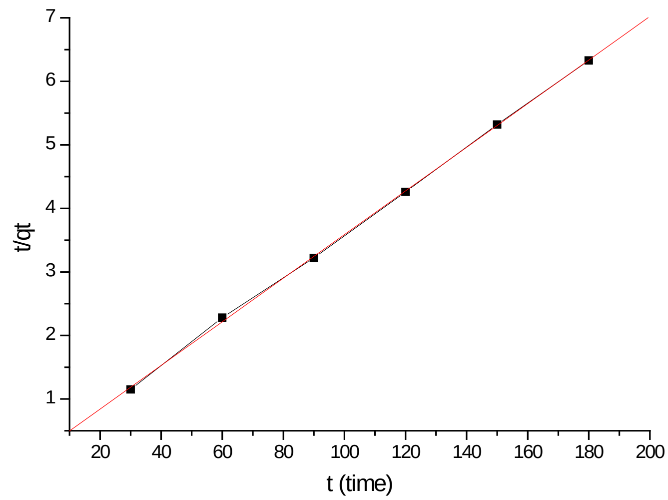

Fig. 9: Pseudo second order kinetics

The adsorption process follows pseudo first order kinetics.

Thermodynamic studies

Enthalpy change (ΔH°), entropy change (ΔS°), free energy change (ΔG°) are thermodynamic parameters. The Langmuir constant K (L/mole) was used to calculate changes in Gibbs free energy according to following equations.

$$\Delta G° = -RT \ln K$$

$$\Delta G° = \Delta H° - T\Delta S°$$

ΔH° andΔS° values can be determined from the slope and intercept respectively from the linear plots ofΔG° vs Temperature (T).

Temp (K)	ΔG (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol)
298	-0.45717	-26.6192	0.0874
303	-0.27941		
313	0.802601		

4. CONCLUSION

The adsorption of CR dye onto groundnut shells was studied. It was concluded that the adsorption of dye increases with increase in pH, contact time, adsorbent dosage, temperature and decreases with concentration of adsorbate. The adsorption isotherms show that based on the R^2 value, Langmuir isotherm is followed. The adsorption isotherm followed second order kinetics. The thermodynamic parameters indicate that the reaction shows chemisorptions.

5. ACKNOWLEDGEMENTS

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REFERENCES

[1] V.K. Gupta,I. Ali, Suhas, and D. Mohan, "Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents", Journal of colloid and interface Science, vol.265, no. 2, 2003, pp.257-264.

[2] I.D. Mall, V.C. Srivastava, N.K. Agarwal, and I.M. Mishra, "Removal of congo red from aqueous solution by bagasse flyash and activated carbon:Kinetic study and equilibrium isotherm analyses", vol.61, no. 4, 2005, pp. 492-501.

[3] I.D. Mall, V.C. Srivastava, N.K. Agarwal, and I.M. Mishra, "Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses,"colloids and surfaces A, vol. 264, no. 1-3, 2005, pp. 17-28.

[4] M.H. Karaoglu,M. Dogan, and M. Alkan, "Removal of reactive blue 221 by kaolinite from aqueous solutions," Industrial and Engineering Chemistry Research, vol. 49, no. 4, 2010, pp. 1534-1540.

[5] C.A. Basar, "Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot," Journal of Hazardous Materials, vol. 135, no. 1-3,2006, pp. 232-241.

[6] G. Crini, "Non-conventional low-cost adsorbents for dye removal: a review," Bioresource Technology, vol. 97, no. 9, 2006, pp. 1061-1085.

[7] Sumanjit and T.P.S Walia, "Use of dairy sludge for the removal of some basic dyes," Journal of Environmental Engineering and Science, vol. 7, no. 5, 2008, pp. 433-438.

[8] M. Koroki, S. Saito, H. Hashimoto, T. Yamada, and M. Aoyama, "Removal of Cr(VI) from aqueous solution by the culm of bamboo grass treated with concentrated sulfuric acid," Environmental Chemistry Letters, vol. 8, no. 1,2010, pp. 59-61.

[9] Q. Sun and L.Yang, "The adsorption of basic dyes from aqueous solution on modified peat-resin particle," Water research, vol. 37, no. 7,2003, pp. 1535-1544.

[10] K.V. Kumar and K. Porkodi, "Batch adsorber design for different solution volume/adsorbent mass ratios using the experimental equilibrium data with fixed solution volume/adsorbent mass ratio of malachite green onto orange peel," Dyes and pigments, vol. 74, no. 3,2007, pp. 590-594.

[11] R. Gong, Y. Sun, J. Chem, H. Liu, and C. Yang, "Effect of chemical modification on dye adsorption capacity of peanut hull," Dyes and pigments, vol. 67, no. 3, 2005, pp. 175-181.

[12] Sumanjit and N. Prasad, "Adsorption of dyes on Rice Husk ash, "Indian Journal of Chemistry-section A, vol. 40, no. 4, 2001, pp. 388-391.

[13] Sumanjit R.K. Mahajan, S. Rani, T.P.S. Walia, and R. Kaur, "Adsorptive removal of five acid dyes using various unconventional adsorbents," Journal of Surface Science and Technology, vol. 26, no. 1-2,2010, pp. 77-93.

[14] J.W Ma, H. Wang,F.Y. Wang, and Z.H. Huang, "Adsorption of 2,4-dichlorophenol from aqueous solution by a new low-cost adsorbent-activated bamboo charcoal," Separation Science and Technology, vol. 45, no. 16,2010, pp. 2329-2336.